UV stable High-Refractive Index Nanocomposites for Extended Reality (XR)

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Abstract
Nanoparticles such as titanium dioxide (TiO$_2$) with high refractive index values of 2.0 in the visible light spectrum are increasingly being sought after for applications in XR waveguide designs for improvements in field of view (FOV). Pixelligent’s PixNIL® formulations with PixClear® TiO$_2$ nanocrystals can create diffractive optical elements and planarized films with refractive index values of up to 2.0 at 520 nm. With the introduction of high refractive index formulations with PixCor™, a new line of nanocrystals using Pixelligent’s proprietary “Core-Shell” technology, we offer significantly improved resistance to near-UV and UVA light exposures in nanoimprintable formulations. The films containing PixCor™ technology maintain very high transparency and low haze in the visible light spectrum and demonstrate high refractive index of 1.9 at 520 nm, and low absorbance, all while maintaining nanoimprintability at commercial scale.

1 Introduction
High-refractive index (HRI) materials have been utilized for improving out-coupling efficiencies in the visible light spectrum optical applications. Reflection losses at the interfaces of index-mismatched optical layers negatively impact overall light extraction efficiencies. XR devices require large FOV to optimize the viewing experience, and one can achieve such large FOVs with HRI optical materials. HRI glass substrates are now commercially available [1] with few options with RI-matching nanomaterials. The combination of HRI materials and index-matching enables next-generation XR devices to arise in the commercial market.

Due to the synthesis and development of both metal oxide nanoparticles and unique formulations comprised of these nanoparticles, major technological gains have been made in enabling HRI optical films for specific applications. Pixelligent’s nanoimprintable PixNIL® formulations (shown in Tables 1 and 2), comprising either PixClear® ZrO$_2$ or TiO$_2$ nanocrystals, have refractive index values that range from 1.7 to as high as 2.0 at 589 nm [2 – 4]. Standard PixNIL® products are available in propylene glycol monoethyl ether acetate (PGMEA) solvent and solvent-free formats, where solvent levels and viscosities dictate film thickness and can cause degradation or adverse reactions with organic materials. This degradation of the surface organics leads to disintegration of the polymers leading to defects, such as yellowing, cracking, unwanted increases in film RI and decreases in film thickness. As the demand for higher refractive index material increases, the need for photochemically and thermally stable TiO$_2$ is becoming essential. With limited organic material options available, inorganic-organic nanocomposite materials remain the only option to attaining such HRI demands.

Table 1. Pixelligent PixNIL® Products and their properties

<table>
<thead>
<tr>
<th>Product</th>
<th>Core</th>
<th>%Solids</th>
<th>Viscosity (cP)</th>
<th>RI (589 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PixNIL® SZ1</td>
<td>PixClear® ZrO$_2$</td>
<td>50%</td>
<td>4</td>
<td>1.7</td>
</tr>
<tr>
<td>PixNIL® SFZ1</td>
<td>PixClear® ZrO$_2$</td>
<td>100%</td>
<td>850</td>
<td>1.7</td>
</tr>
<tr>
<td>PixNIL® ST1</td>
<td>PixClear® TiO$_2$</td>
<td>50%</td>
<td>3</td>
<td>1.8</td>
</tr>
<tr>
<td>PixNIL® ST2</td>
<td>PixClear® TiO$_2$</td>
<td>50%</td>
<td>3</td>
<td>1.9</td>
</tr>
<tr>
<td>PixNIL® STF1</td>
<td>PixClear® TiO$_2$</td>
<td>100%</td>
<td>700</td>
<td>1.9</td>
</tr>
<tr>
<td>PixNIL® ST5</td>
<td>PixClear® TiO$_2$</td>
<td>50%</td>
<td>4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 2. Examples of dilutions of PixNIL® ST2 Products and their film thickness ranges.

<table>
<thead>
<tr>
<th>Product</th>
<th>%Solids</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PixNIL® ST2E</td>
<td>10%</td>
<td>50 – 300 nm</td>
</tr>
<tr>
<td>PixNIL® ST2A</td>
<td>15%</td>
<td>100 – 400 nm</td>
</tr>
<tr>
<td>PixNIL® ST2</td>
<td>50%</td>
<td>500 nm – 2.0 μm</td>
</tr>
<tr>
<td>PixNIL® ST2B</td>
<td>70%</td>
<td>&gt; 2.0 μm</td>
</tr>
</tbody>
</table>

TiO$_2$ has generated much interest for optical applications because of its high refractive index. When combining 20-nm TiO$_2$ nanoparticles with monomers, oligomers and other resin ingredients, resultant films can have high transparency and high refractive index. PixNIL® products comprised with PixClear® TiO$_2$ nanocrystals have demonstrated utility for many applications, but limitations in certain applications can exist at specific wavelengths. It is quite well-known that TiO$_2$ particles absorb specifically UV light and are photocatalytic. The energy band gap for anatase and rutile are 3.23 or 3.06 eV, respectively. As a result of this, TiO$_2$ is photochemically active and can cause degradation or adverse reactions with organic materials. This degradation of the surface organics leads to disintegration of the polymers leading to defects, such as yellowing, cracking, unwanted increases in film RI and decreases in film thickness. As the demand for higher refractive index material increases, the need for photochemically and thermally stable TiO$_2$ is becoming essential. With limited organic material options available, inorganic-organic nanocomposite materials remain the only option to attaining such HRI demands.

Certain mitigation measures could be administered to
work around this photocatalytic behavior. For example, applications involving long wavelength infrared (IR) light exist for optical sensors and function well above the UV wavelength range. Hence, under this type of application the photocatalytic reaction cannot occur, leaving optical film properties intact and stable. Other mitigation strategies involve blocking and absorbing agents specific to the wavelengths of UV light. Such options tend to be additional blocking layer place upon the TiO2 nanocomposite film layer or special additives to the nanocomposite formulation that prevent UV photons from reaching the TiO2 surfaces. A different mitigation process involves passivating the TiO2 nanocrystal surfaces with layers that suppress the photocatalytic activity.

Figure 1. (Top Left) Slanted gratings with 51° angle, 1.8:1 aspect ratio and 450 nm residual layer thickness using PixNIL® ST6 (Base of grating is approximately 100 nm); (Top Right) 130-nm slanted gratings with 55° angle and 50-nm residual layer (line added as a guide, residual layer thickness is between the two lines). (Bottom) DOE of PixNIL® ST2; Courtesy of NIL Technology and SCIL Nanoimprint Solutions.

Pixelligent’s PixCor™ TiO2/ZrO2 nanocrystals are being developed to address photocatalytic behavior of TiO2 to provide a solution to this problem while maintaining adequate optical and NIL properties. A ZrO2 shell is deposited onto the TiO2 nanocrystal (see Figure 2), leading to a 25-nm hydrodynamic diameter nanocrystal after capping of the shell. Dynamic light scattering (DLS) curves, like the one in Figure 2, show that uniform, narrow particle size distribution with no aggregation have been achieved like other PixClear® TiO2 and ZrO2 nanocrystals. When formulated with acrylic resin ingredients, PixCor™ has demonstrated the same compatibility as PixClear® TiO2 in PixNIL® formulations in similar resin systems. PixCor™ is developed to perform like PixNIL® products with the added benefit of improved UV stability coming from the ZrO2 shell.

Figure 2. (Left to Right) TEM of TiO2 Core, PixCor™ TiO2/ZrO2 nanocrystal schematic, TEM of ZrO2 on the same TiO2 nanocrystals as the one on the left, Dynamic Light Scattering (DLS) of PixCor™ nanoparticle size.

Other Pixelligent nanocomposite formulations have been developed for specific deposition applications in addition to spin-coating and NIL, such as inkjet printing for OLED display devices. Pixelligent’s PixJet® formulations have been tailored to be solvent-free, low-viscosity, and appropriate for high-throughput, continuous-use industrial inkjet-printing while yielding films with uniform thickness and 1.65 RI at 589 nm. PixJet® SFZ5 offers exactly these properties to OLED display customers. When looking beyond OLED display applications, PixJet® formulations can be tailored for other applications including: micro lens deposition and “jet coating” dispensing techniques for >20 cP inks. Of particular interest for future opportunities, there are low-viscosity routes to achieving reduced residual layer thickness and likely UV-stable preferences in which PixCor™ enabled formulations with > 1.7 RI are required.

In this manuscript we share UV exposure results and NIL data for a new 1.9 RI PixCor™ formulation, showing the benefits for Pixelligent’s PixCor™ nanocrystals.

2 Experiment and Methodology

2.1 Formulating

Test formulations consist of UV-curable acrylates as the base resin referred to as “Resin 1” for the nanocrystals in PGMEA solvent, and the nanocrystals used were PixClear® ZrO2, PixClear® TiO2, and PixCor™ nanocrystals. TiO2 has the greatest photocatalytic activity of the three while ZrO2 is the least photocatalytic. Therefore, our PixCor™ nanocrystal will be compared to these two photocatalytically different nanocrystals to show how our PixCor™ technology allows for a reduced color change, better film RI and thickness retention, and no losses in film clarity.

2.2 Film Making

Spin-coating onto Glass Substrates

Films were spin-coated on precleaned 2.5”x 2.5” soda lime glass. The standard processing conditions for solvent containing formulations have a prebake or soft bake prior to the UV cure performed on a hot plate. The prebake (or soft bake) condition of 50 C/5 min is intended to remove residual PGMEA after the spin-coating step. The films are UV cured using a 365-nm UV LED source with 125 mW/cm2 intensity in an inert (N2) environment. The postbake (or hard bake) condition of 100 C/5 min is performed in an oven after cure to complete the cure and remove any residual volatiles. The targeted film thickness was 1 micron for this study.

2.3 UV Exposure Conditions

405-nm UV Exposure

PixCor™, PixClear® TiO2, and PixClear® ZrO2 are tested for the photostability to 405 nm UV light under a specific intensity and exposure time. The internal UV setup comprises of lamps of desired wavelengths and a flat aluminum tray placed on a rotating turntable for uniform exposure. The lamps are placed above the test film samples by approximately 6 – 12 inches with the film
surface facing upwards. The aluminum tray is then spun at a slow speed while the films are exposed to the light for the desired duration. Nanocomposites are exposed to UV light at an average intensity of (25 mW/cm²) for 148 hours (total UV dosage of 13,000 J/cm²). The optical properties of the nanocomposites film properties such as L*, a*, b*, %Haze, film RI and film thickness before and after the total exposure are measured and recorded.

2.4 Measurements
Each film was measured using a HunterLab Vista spectrophotometer under 400–700 nm. This tool measures the average color parameters L* (whiteness/blackness), a* (red/green) and b* (blue/yellow) as well as the %Haze of the films. Color changes are calculated using \( \Delta E^* \), which is a calculated value that accounts for changes in the color parameters. The equation is shown below (Eq.1)

\[
\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\]  

Equation 1

Refractive index and film thickness of each film were measured using Metricon Model 2010/M prism coupler with 448 and 635 nm wavelength lasers. Film thickness changes were tracked by comparing values before and after exposure to UV conditions. RI values at 520 nm were calculated using a modified Cauchy equation discussed in previous papers [2].

2.5 Nanoimprinting
PixCor™ Resin 1 was sent to UMass/Amherst for nanoimprinting. SEM photos were proved as visual verification of imprinted structures and will be included in the data section. Two structure types are shown: 500-nm binary gratings and 800-nm metalenses with approximately an 8:1 aspect ratio.

3 Data
Before discussing UV exposure data for the three film types (PixClear® ZrO2, PixClear® TiO2 and PixCor™), it is important to review initial film properties. In Table 3 the three films are compared by b* (initial color), film RI (influence of nanocrystal type at the same loading), film thickness and film %Haze (level of film clarity).

<table>
<thead>
<tr>
<th>Initial Properties</th>
<th>PixClear® ZrO2</th>
<th>PixClear® TiO2</th>
<th>PixCor™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film b*</td>
<td>0.30</td>
<td>1.50</td>
<td>0.60</td>
</tr>
<tr>
<td>Film RI (520 nm)</td>
<td>1.73</td>
<td>1.91</td>
<td>1.88</td>
</tr>
<tr>
<td>Film Thickness (µm)</td>
<td>0.99</td>
<td>0.92</td>
<td>1.07</td>
</tr>
<tr>
<td>Film Haze (%)</td>
<td>0.10</td>
<td>0.20</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Due to the presence of near-UV and blue light absorbers in the films, a typically positive b* value results. Certain absorbers can be photoinitiators since they can absorb around 400 nm light and can contribute to positive b* values. PixClear® ZrO2 has relatively low near-UV/blue absorption and has the lowest value of the sample set at 1 micron. Because of the absorptive behavior of TiO2 at short wavelengths, we would expect the PixClear® TiO2 film to have a higher b* value than PixClear® ZrO2 as it is shown. The PixCor™ film exhibits an intermediate b* value because the ZrO2 shell suppresses some of the near-UV/blue light absorption during the measurement.

The film RI at 520 nm values differ among the three films and are obviously dependent upon the nanocrystal type. PixClear® ZrO2 and PixClear® TiO2 in Resin 1 have the lowest and highest RI values of 1.73 and 1.91, respectively. PixCor™ has an RI of 1.88 which is quite close to that of PixClear® TiO2. This observation implies that the ZrO2 shell does not diminish the overall RI of the TiO2 core significantly, but it is understood that some trade-off in RI is expected.

Finally, the film haze is measured as an indicator of compatibility of the nanocrystals with the components of Resin 1. Indicators of incompatibility are often apparent when nanocrystal aggregation and separation occurs. Film data with high %Haze for a given film thickness would be suggestive of nanocrystal aggregation. Often values > 1% are indicative of undesirable film haze. All three films with each nanocrystal have low haze values that are approximately equivalent to each other, showing good transparency.
Figure 3. Graphs showing changes in film properties a.) \(\Delta E^*\), b.) \(\Delta RI\), c.) \(\Delta Film Thickness\), and \(\Delta \%Haze\) after exposing cured films to 405 nm light for 148 hours. All nanocrystals were formulated in Resin 1 with the same ratios.

The quantitative measurements used for measuring UV stability were \(\Delta E^*\), \(\Delta RI\), \(\Delta Film Thickness\) (in microns) and \(\Delta \%Haze\). As described in equation 1, a \(\Delta E\) combines color parameters \(L^*\), \(a^*\) and \(b^*\) to give a more representative number for overall color change, although films will mostly show increases in yellow color (\(b^*\)). For reference, a \(\Delta E^*\) of less than 1 is one that is not perceptible to the human eye [5]. Figure 3a shows the reduction of overall cured film color change in the PixCor™ formulation as compared to PixClear® ZrO2 and PixClear® TiO2 in Resin 1. PixClear® ZrO2 is the least photocatalytic and did not register any significant change in color. Both the PixClear® TiO2 and PixCor™ films showed color changes, but it is the PixCor™ that displayed \(\Delta E^* < 0.6\). Again, the ZrO2 shell is effective in passivating the TiO2 core and dampening the photocatalytic reaction.

The film RI and thickness are connected and could change together under certain conditions. This can be seen in Figure 3b and 3c for the three film types. Again, PixClear® ZrO2 performs the best with little change in both film RI and thickness after UV exposure. The PixCor™ film RI increased by roughly 0.03 with a corresponding film thickness decrease of 0.1 microns or 100 nm. These changes represent some loss of organics within the film and film shrinkage due to some photocatalysis over time. Under the same UV exposure, the PixClear® TiO2 exhibits the largest change in film RI and thickness that are approximately twice as much as the PixCor™ film.

As a final property in monitoring film changes, the %Haze was measured after UV exposure. One can see in Figure 3d that all three films have relatively low changes in film haze of <0.2% that are not overly significant. However, the PixClear® TiO2 film is developing a noticeable final haze around 0.5% that could be indicative of film crack formation and may introduce scattering effects. The PixClear® ZrO2 and PixCor™ films changed very little by comparison to the PixClear® TiO2 with final %Haze values still <0.2%.

Samples of PixCor™ Resin 1 were sent to our partners at UMass/Amherst for SEM photos to assess nanoimprint lithography capabilities. Figure 4 below shows two types of imprints with different aspect ratios. Both types of imprint structure showed good fidelity and low residual thickness layers (marked by the red arrows) of approximately 100 and 200 nm, respectively. These imprints are not optimized, and further work will continue to refine the NIL process.

Figure 4. Nanoimprints of PixCor™ in Resin 1-Courtesy of UMass Amherst. The Residual Layer Thickness (RLT) is captured with the red arrow. From left to right, RLT of the figure on the left is ~100nm and 200nm respectively.

4 Results and Conclusions
The information in this manuscript highlights that our PixNIL® formulations have demonstrated optical properties and NIL capabilities that can drive XR applications further. The addition of our UV-stable PixCor™ formulations to the Pixelligent product portfolio can add to the existing benefits of HRI materials. After 405-nm UV exposure films made from our PixCor™ 1.9 RI formulation exhibits a reduced color change (\(\Delta E^* = 0.5\)) in comparison with PixClear® TiO2 (\(\Delta E^* = 1.2\)). The data also shows that PixCor™ has good refractive index and film thickness retention with a change of 0.03 and 0.1 um, respectively after UV exposure. The PixCor™ film maintains good film integrity and clarity after UV exposure. PixCor™ formulations show encouraging nanoimprint capabilities with simple binary and high-aspect ratio gratings. Additionally, this formulation has the ability to achieve low residual layer thicknesses of 100 to 200 nm.

References


